AN EXPLORATORY ION PROBE SEARCH FOR ^{54}CR-RICH GRAINS IN ORGUEIL. U. Ott[1], S. Specht[1] and F. A. Podosek[2], [1]Max-Planck-Institut für Chemie, Becherweg 27, D-55128 Mainz, Germany (e-mail: ott@mpch-mainz.mpg.de), [2]McDonnellCenter for the Space Sciences, Washington University, St. Louis, Mo. 63130-4899, USA.

Summary: One hundred and twenty-one chromium-rich grains in a partially dissolved sample of the Orgueil meteorite were analyzed by ion microprobe for the isotopic composition of their Cr. Most compositions were found to be indistinguishable from normal within the often large analytical uncertainties for the analysis of such small (≤ µm) grains. A number of grains, however, show enhanced ^{54}Cr/^{52}Cr, with the effect ranging up to nominally >70%. In spite of the large errors, statistical fluctuations are an unlikely explanation. The exact identity of these grains, which may be the source of the smaller ^{54}Cr enhancements observed in solutions analyzed by thermal ionization mass spectrometry, remains to be established.

Introduction. Unique (so far) among the established isotope abundance anomalies in meteorites is the ^{54}Cr anomaly observed during sequential dissolution of primitive meteorites [1-4]. Unlike other isotope abundance anomalies, it can neither be linked to Ca-Al-rich inclusions [5,6] nor to surviving interstellar material [7-10] of mostly carbonaceous type or to other carbonaceous materials [11,12]. It has been most clearly seen in the Orgueil meteorite, where the >80% of the Cr most easily dissolved show a small (~6 ε-units) negative ^{54}Cr anomaly, while analyses of the remainder yield positive anomalies in the percent range. In previous work only solutions were analyzed (by TIMS) so that any direct information regarding the phases carying the anomalies was lost. It therefore seemed worthwhile to perform a direct search for ^{54}Cr-rich grains using the ion microprobe. Here we report on the results of such an exploratory search. Key to the approach was the suggestion - based on the lack of observed correlated anomalies in other elements - that (a) Cr-rich phase(s) may be the carrier(s) of excess ^{54}Cr [4].

Samples. For the ion probe work the residue from treatments with acetic and nitric acid (that, according to the earlier work, dissolve >80% of the Cr) was magnetically separated in NaOH, and the non-magnetic fraction split in a ratio ca. 60:40. The larger part was further treated with HCl, which yielded solutions with ^{54}Cr/^{52}Cr enhanced by up to 2.1% [4]. Material from the smaller split was suspended in water and deposited on gold foil for ion microprobe analysis. The sample mounts were inspected by SEM and numerous submicron- to micron-size Cr-rich grains were found. In the EDX analyses, most of these grains showed, besides Cr, only oxygen and small amounts (few percent) of Fe; a few grains with no detectable Fe were also seen. Besides the grains identified in the SEM, additional grains found in the ion probe were also analyzed for their Cr isotopic composition.

SIMS isotope analyses. Cr was measured as Cr^+ ions produced by bombarding the grains with a primary O^- beam. Special consideration had to be given to grain lifetime and a low intensity primary ion beam of only ~0.2 nA was used. About half of the analyses were performed at mass resolution >6100, sufficient to resolve $^{54}Cr^+$ from $^{53}CrH^+$. The other half was measured at lower resolution (between 3800 and 5800), not sufficient for nominal hydride resolution. Since ^{53}Cr would have been more affected - both because of the required mass resolution and the relative abundances of Cr isotopes -, and no evidence for apparent enhancements at mass 53 was found (see below), we conclude that, within the analytical uncertainties of the measurements, hydride interferences were of no consequence also at mass 54. Inconel alloy 601 was used as an isotopic standard placed on the same sample mount as the grains to be analyzed. Counting times at the individual isotopes were chosen so that expected errors based on counting statistics were about equal for ^{53}Cr/^{52}Cr and ^{54}Cr/^{52}Cr and about 1.4x higher for ^{50}Cr/^{52}Cr. Corrections for isobaric interferences from ^{50}Ti (insignificant) and ^{54}Fe were applied based on measured signals at masses 48 and 56, resp.. A few analyses with strongly varying elemental ratios are omitted from the following discussion.

Results and Discussion. Most of the grains analyzed are indistinguishable from normal within error in all three isotopic ratios. However, a closer look reveals significant differences between ^{54}Cr/^{52}Cr and the two other isotopic ratios. The distribution of ^{50}Cr/^{52}Cr and ^{53}Cr/^{52}Cr ratios is essentially compatible with a statistical distribution around the normal values. This is obvious from a look at the ratios that deviate by more than 2σ from normal (Fig. 1). Out of the 122 analyses of 121 grains, 8 differ by more than 2σ from normal in ^{50}Cr/^{52}Cr, as do 12 of the ^{53}Cr/^{52}Cr ratios; 1 and 4, resp., differ by more than 2σ from the range defined by the dashed lines, which show the ±2σ standard deviation of the standards. For ^{54}Cr/^{52}Cr the situation is completely different: twenty-six out of 121 ratios differ from normal by more than 2σ, and the majority of these (17) also from the range defined by the standards. In addition, while the distribution of 2σ-"outliers" is essentially symmetric in the case of ^{50}Cr/^{52}Cr and ^{53}Cr/^{52}Cr, all but two of the twenty-six ^{54}Cr/^{52}Cr "outliers" show enhancements. The ion ratio $^{56}Fe^+/^{52}Cr^+$ of the standard was approximately 0.1, similar to what was typically encountered in the analyses of the meteoritic grains, hence we are confident that corrections for isobaric interferences from ^{54}Fe were reliable (normal $^{54}Fe/^{56}Fe$ provided) and that our data indicate the widespread occurrence of Cr-rich (Cr oxide?) grains with high ^{54}Cr.

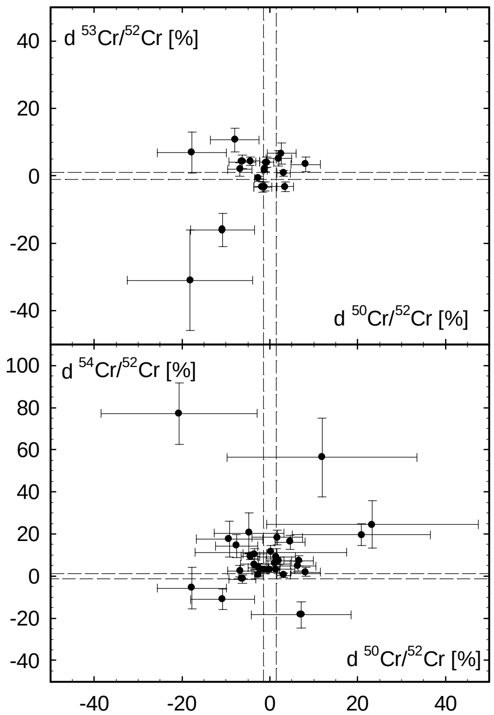

Fig.1.: Three-isotope plots of d $^{53}Cr/^{52}Cr$ (top) and d $^{54}Cr/^{52}Cr$ (bottom) vs. d $^{50}Cr/^{52}Cr$, where d $^{i}Cr/^{52}Cr$ gives the deviation from normal in %. In order not to clutter the diagrams, only those data points are shown that in at least one of the ratios plotted deviate from normal by $\geq 2\sigma$. Error bars are 1σ. Dashed lines show the $\pm 2\sigma$ standard deviations for the standards.

Fig. 2 is a plot of $^{54}Cr/^{52}Cr$ ratios vs. the sum of $^{52}Cr^{+}$ registered used as a rough measure of grain size. All data points are shown in the upper part of Fig. 2, while the lower part shows the 2σ-"outliers" only. Nominal ^{54}Cr enhancements are highest for some of the "smallest" grains, ranging up to >70%, but also some of the "larger" grains show enhancements of several percent. Summation of all grains analyzed - weighted by count rates - yields an "integrated" $^{54}Cr/^{52}Cr$ that is higher than normal by 1.8%, which - given the uncertainties involved in this rough estimate - is fully compatible with what would be expected based on the analyses of solutions in earlier experiments [4].

In the grain data presently available, no correlation of $^{54}Cr/^{52}Cr$ with other properties is discernible. However, there is some indication that our grain analyses are still compromised by a finely disseminated background from the solutions. This is indicated, e.g., by the fact that the Fe/Cr ratios seen in the ion probe are invariably higher than those seen in point analyses of grains by SEM/EDX. It cannot be excluded that such a dilution effect also effects the Cr isotopic analyses and that a small fraction of fine grains may show much larger ^{54}Cr enhancements than typically reported here. Improved separation and analysis techniques will be required for further progress.

Acknowledgments. We thank St. Richter and Ch. Sudek for help with the grain search in the SEM.

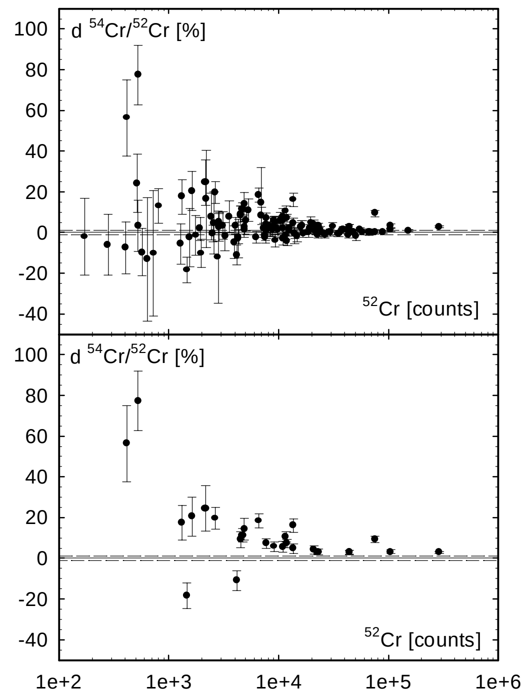

Fig.2: Deviations of $^{54}Cr/^{52}Cr$ from normal [%] plotted vs. total measured counts of ^{52}Cr as a rough indicator of grain size (top: all grains; bottom: only grains that deviate from normal by $>2\sigma$). While the nominally largest effects are seen for low ^{52}Cr with large errors, also some "larger grains" show enhanced $^{54}Cr/^{52}Cr$. Errors shown are 1σ. Dashed lines show the $\pm 2\sigma$ standard deviations for the standards.

References: [1] Rotaru M. et al. (1992) *Nature* **358**, 465. [2] Ott U. et al. (1994) *LPS* **XXV**, 1033. [3] Podosek F. et al. (1995) *Meteoritics* **30**, 562. [4] Podosek F. et al. (1996) *Meteoritics and Planet. Sci.*, subm. [5] Lee T. (1988) in: *Meteorites and the Early Solar System*, 1063. [6] Papanastassiou D.A. (1986) *Ap.J.* **308**, L27. [7] Ott U. (1993) *Nature* **364**, 25. [8] Anders E. and Zinner E. (1993) *Meteoritics* **28**, 490. [9] Nittler L. et al. (1994) *Nature* **370**, 443. [10] Nittler L. et al. (1995) *Ap.J.* **453**, L25. [11] Zinner E. (1988) in: *Meteorites and the Early Solar System*, 956. [12] El Goresy A. et al. (1995) *Nature* **373**, 496.